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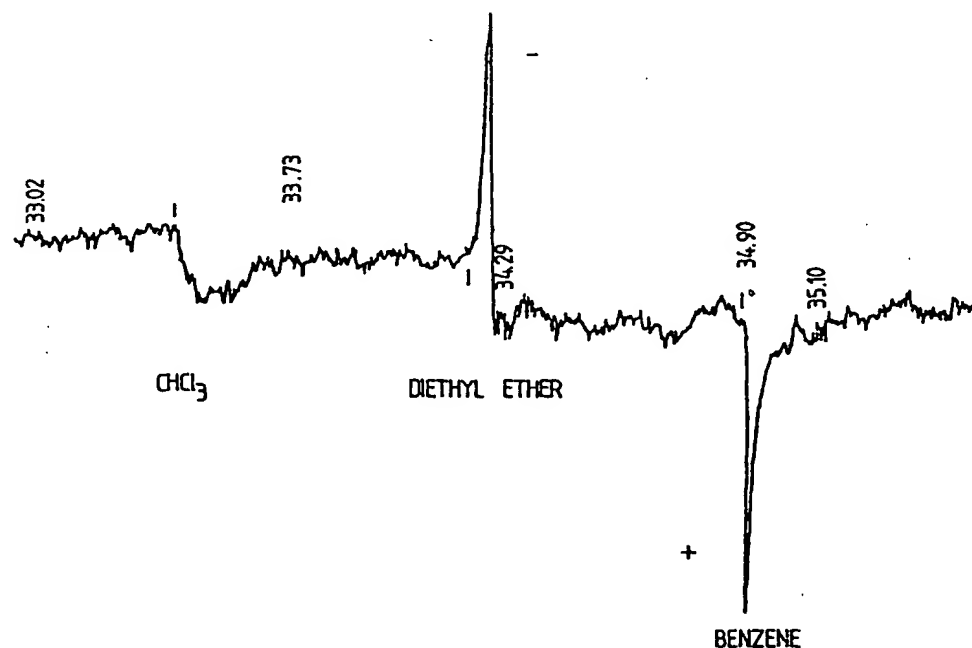
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(54) Title: GAS SENSORS, AND METHODS OF MAKING AND USING THEM



(57) Abstract

A sensor for gases, vapours, odors, etc. has an organic polymeric semiconductor element which changes its electrical resistance in the presence of certain gases. The polymere is formed by electrolytic deposition on the substrate from a solution of its monomer, the solution comprising a solvent medium in which the monomer is sparingly soluble, a protic solvent, and an ionic base. A number of different gas detectors can be used to obtain from each a characteristic response to the presence of a gas, and the combination of responses can be used to distinguish between gases. The different detectors

GAS SENSORS, AND METHODS OF MAKING AND USING THEM

The invention relates to gas sensors. The term "gas" in this context includes materials which are gaseous under normal conditions, as well as vapours and odours.

Many types of sensors for gases based on different detection principles are now available. They include thin film lanthanide oxide semiconductors, surface acoustic wave devices, pyroelectric enthalpimetric sensors based on thermally programmed desorption, and new sensors based on field effect transistors coated with gas sensitive substances, for example lanthanum oxide. None of these sensors are particularly satisfactory as they tend to lack specificity, for example lanthanide oxide semiconductors respond to any reducing gas, need to work at high temperature in order to have reasonably fast responses, and are easily poisoned. Other methods require complex and expensive instrumentation. New techniques using field effect transistors are potentially very useful since they combine small size with sensitivity, but the problems of selectivity are yet to be resolved.

Sensors are described in EP 22028 A1, based on organic semiconductor materials of which polypyrrole and polychloraniline are mentioned. In particular the electrolytic deposition of polypyrrole on an electrode from a solution of pyrrole sulphate is described.

The sensors described in EP 22028 are stated to

respond, by change in electrical resistance, to the group of gases evolved during combustion i.e. CO, CO₂, NO, NO₂, HCl, NH₃, HCN and SO₂; and particularly the gases evolved when cellulose burns with or without a flame, or when alcohol
5 burns. The sensors are further described as responsive to a further group of gases namely, hydrogen, methane, propane and butane.

However, EP 22028 only discloses gases which produce a response in decreasing the resistance of the sensor material.
10 No disclosure is made of gases which do not alter or which increase the resistance of the sensor material, or that a gas might increase the resistance of one material, while decreasing the resistance of another material.

Furthermore, the sensor materials are in general used
15 singly; and although it is suggested that they can be linked in series or parallel, and indeed two examples of parallel linking of two sensor materials are given, only a single output signal is obtained, and there is no suggestion of observing the signals separately: the aim of combining them
20 being to get a response from the range of gases to be detected, rather than to distinguish between individual gases. This further reinforces the apparent expectation of getting only one type of reaction; namely, a decrease in resistance of the sensor material. In addition the
25 formation of organic polymeric sensors is but poorly described.

The present inventors have unexpectedly discovered

that gases can have quite different responses with a range of sensor materials; increasing, decreasing or having negligible effect on the conductivity of the sensor material, and this can be put to use in differentiating
5 between gases, and even identifying a gas, either absolutely or as a member of a specified group of gases.

A gas sensor of the present invention is characterised in that it employs at least one polymeric organic semiconductor material the electrical conductivity of which in
10 the presence of the gas to be detected undergoes a change enabling identification of the same.

The sensor can be further characterised according to one preferred form of the invention by the use of a plurality of different semiconductor materials whose
15 reactions to the gas under test are separately taken, giving a response spectrum characteristic of the gas to be detected so enabling identification of the same.

According to another preferred feature of the invention the sensor is used in conjunction with another
20 detection system to discriminate between a plurality of possible alternatives for the gases detected by said other detection system. Said other detection system may be another sensor of the present invention, or it may be a different system such as a flame ionisation detector.

25 The invention is further characterised in that it provides novel organic polymeric semiconductor materials having electrical properties useful in such sensors. The

materials novel per se comprise: polythiophene-2-acetonitrile; polyisobutylthiazole; polyindole; polydimethylaniline; polyphenol; polymethylpyrrole; polyphenylenediamine; polyisovaleraldehyde-aniline (Schiff's base);
5 polymethylaniline; polyhexylaniline; polyanilinoethylacetate; polyanilinomethylbutylacetate; and polyanilino-menthylacetate. However, the present invention provides novel methods of preparing such polymers, as described more fully below, which seems to influence the gas-sensitivity
10 characteristics of the polymer. The polymers thus produced are novel per se over known polymers which are nominally the same, such as polypyrrole and polychloroaniline, but which evidently differ structurally in some manner.

The element may comprise more than one material. For
15 example, one material may be a substrate supporting another material. A preferred substrate is polypyrrole which may support any other material of the group. The supported material is preferably a coating on the substrate.

The element is preferably formed by electrolytic
20 deposition. The material or at least one of the materials of the element is preferably deposited onto a metallic electrode. The electrode may, for example, be of platinum which may be wire, tape, mesh, plate or other form. A preferred form of electrode comprises two adjacent wires
25 onto both of which the material is deposited to form a body of material bridging the wires.

A method of making a gas sensor, according to the

invention, is characterised by electrolytically depositing a semiconductive organic polymer material onto a substrate electrode using as electrolyte a solution of a monomeric form of the material in a solvent in which the monomer is sparingly soluble.

Embodiments of sensors and methods of making and using them will now be described by way of example to illustrate the invention with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram showing a basic form in which any of the sensors described may be made;

Figure 2 is a schematic diagram of a circuit suitable for use in measuring the response of the sensors described;

Figures 3 and 4 are traces obtained with the embodiments of E and A respectively, using the circuit of Figure 2 showing changes in electrical resistance plotted as ordinate for ambient atmospheres of different gases specified at positive or negative peaks along the abscissa;

Figure 5 is a table listing gases in a vertical column to the left with the corresponding increases or decreases in resistance exhibited by the five embodiments A to E indicated by "+" or "-", respectively, in five columns to the right. The designation "0" indicates negligible response.

Figure 6 is a table showing the solvent used in making embodiments F to W with comments on polymerisation; and

Figure 7 is two traces, the upper being the response

from a flame ionisation detector to (a) ethanol and (b) iso-octane and the lower a resistance characteristic response to (c) ethanol for a polychloroaniline sensor according to the invention.

5

Materials and methods of making preferred embodiments

The general procedure for electrolytic formation and deposition of the polymeric semiconductor materials hereof is as follows.

The monomer is dissolved in solvent medium in which it is sparingly soluble and which comprises a protic material for creating ions, and will normally comprise also an aprotic solvent miscible with the protic material for the purpose of creating the appropriate solubility conditions for the monomer and polymer. An ionic base may be dissolved in the solvent medium to act as electrolyte and counteract negative ions in the polymer. The amount of ionic base used will affect the electrical properties of the polymer, and can be varied accordingly. In general, increasing the amount of base will decrease the concentration of delocalised electrons in the polymer and therefore increase its resistance. On the other hand, it could make the polymer more sensitive to disturbance of the remaining electrons by the gas being detected, and hence increase the sensitivity of the device. Suitable bases are the quaternary amines, for example tetraethylammonium-

tetrafluoroborate. The protic medium will usually be water; and the aprotic solvent can be selected according to the solubility characteristics of the monomer, but will usually be found among common aprotic solvents such as acetonitrile, tetrahydrofuran, dimethoxyethane, ethanol and acetone.

The electrolytic conditions are selected in order to obtain a satisfactory deposit. The voltage will have to be above the natural energy barrier of the electrolytic medium, typically about 1.2 volts. With a small overvoltage a thin, shiny deposit of polymer is usually produced - probably a monomolecular layer - which has of course a very high resistance. As the overvoltage is increased, the polymer is deposited in a more finely divided form, as a thicker layer, with therefore a larger surface area and lower resistance, and probably shorter polymer molecules. The voltage can therefore be selected to control these characteristics of the polymer. As will be seen from the examples about 3 volts gives acceptable results in many cases. The current flowing will depend inter alia on the physical dimensions of the electrodes, so that the configuration and spacing of these can be used to control the current to a desired level. Usually a few microamps is sufficient to obtain an adequate deposit in a reasonable time. If the current is too high, the deposit will tend to be unstable, while if it is too low, it will take too long to form.

In Examples A to E, pyrrole, 2-chloroaniline, thiophene-2-acetonitrile, indole and tetraethylammonium-

tetrafluoroborate were from Fluka AG, Switzerland.
2-isobutylthiazole was from Oxford Organic Chemicals Ltd.,
Brackley, UK. These compounds were redistilled or
recrystallised before use.

5

A. to E. Sensors based on polymers deposited on
a platinum electrode substrate

A. Polypyrrole

10 Polypyrrole was synthesised electrolytically by
deposition on a platinum anode. This consisted of two
platinum wires of 0.1 millimetres diameter placed 0.2 mm
apart. The polymer was deposited so that a conductive layer
was formed between the two wires of the anode (Fig. 1). The
15 cathode consisted of a single platinum wire of 0.1 mm
diameter. The electrolyte consisted of 0.1M pyrrole/ 0.1M
tetraethylammoniumtetrafluoroborate in 99% acetonitrile, 1%
water. The distance between the anode and cathode was 1.5
centimetres and the conductivity of the electrolyte was 9.1
20 - 9.5×10^{-7} mho. Electrolysis was carried out for 20
minutes at a constant voltage of 3 volts. The current
during the time of electrolysis fell from 8 μ A to 3 μ A as
deposition of polypyrrole occurred on the anode. The sensor
was washed in acetonitrile and dried in air and had a
25 resistance of 400 - 700 ohms.

B. Poly-2-chloroaniline

Polychloroaniline was synthesised electrolytically on

to the surface of a pyrrole sensor (A) again by anodic deposition. The electrolyte consisted of 0.1M 2-chloroaniline/0.1M tetraethylammoniumtetrafluoroborate in 90% ethanol, 10% water. This solution had a conductivity of 1.25×10^{-4} mho and the cell dimensions were identical to (A). Electrolysis was carried out for 10 minutes at 3V. The resulting sensor was washed in ethanol, dried in air and had a resistance of 1-8 Mohm.

C. Poly-2-acetonitrile

Polythiophene-2-acetonitrile was synthesised electrolytically on to the surface of a pyrrole sensor (A) by anodic deposition. The electrolyte consisted of 0.1M thiophene-2-acetonitrile/0.1M tetraethylammoniumtetrafluoroborate in 80% ethanol, 20% water. The solution had a conductivity of 1.1×10^{-5} mho. Electrolysis was carried out for 10 minutes at 3V. The resulting sensor was washed in ethanol and when dry had a resistance of 300-800 ohm.

D. Poly-indole

Polyindole was synthesised electrolytically on to the surface of a pyrrole sensor (A) by anodic deposition. The electrolyte consisted of 0.1M indole/0.1M tetraethylammoniumtetrafluoroborate in 84% ethanol, 16% water. This solution had a conductivity of 2×10^{-5} mho. Electrolysis was carried out for 10 minutes at 3V. The resulting sensor was washed in ethanol and when dry had a resistance of 1-5 Kohm.

E. Poly-2-isobutylthiazole

Polyisobutylthiazole was synthesised electrolytically on the surface of a pyrrole sensor (A) by anodic deposition. The electrolyte consisted of 0.1M 2-isobutylthiazole/0.1M tetraethylammoniumtetrafluoroborate in 99% acetonitrile, 1% water. The conductivity of this solution was 6×10^{-7} mho and electrolysis was carried out for 10 minutes at 3V. The resulting sensor was washed with acetonitrile and when dry had a resistance of 150-600 ohm.

In embodiments B to E, it will be seen that a two-layer sensor is formed, with polypyrrole as the first layer and the other polymer deposited on top of it. This was primarily because polypyrrole binds strongly to platinum, and therefore provides a better substrate for depositing the other polymer. However, it has also been found that the resulting sensor can have different properties from either of the component polymers applied singly.

Other organic polymer materials can be used instead of those described especially materials which are compounds with large amounts of pi-electron delocalisation.

Each sensor was completed as shown in Figure 1. The two platinum anode wires 10 were enclosed in respective glass capillary tubes 12,14 secured side by side to one another to give a strong mechanical support. The element 16 of polymer material is exposed immediately adjacent the lower ends of the tubes 12,14. The element 16 forms the sensor resistance shown in Figure 2.

The change in electrical resistance on exposure to

different gases was measured using the simple circuit of Figure 2.

In Figure 2 the circuit components have the values as follows: $R_1, R_2 = 18 \text{ kohms}$; $R_3, R_4 = 56 \text{ kohms}$; $VR_1 = 100$
5 kohms. The output was used to drive a chart recorder having a chart speed of 8 cms per minute and set to a sensitivity of 0.64 millivolts per cm for Figure 3 and 1.28 mV/cm for Figure 4.

In Figures 3 and 4 negative and positive resistance
10 changes are indicated by upward and downward excursions of the trace, respectively.

The sensors made according to examples A to E showed good mechanical strength, were electrically stable over a period of several months and were not poisoned by any of the
15 compounds tested. Examples of the electrical response to different compounds is given in Figures 3 and 4, which show resistance characteristics having specific shape features by which corresponding respective compounds can be identified. The changes in electrical resistance on exposure to differ-
20 ent compounds were investigated and these are summarised in Figure 5. With some sensors increased resistance was observed while with others a decrease in resistance was observed to the same compound. For example on exposure to ammonia sensors B and D showed a decrease in resistance
25 while A, C, E showed an increase in resistance.

Differentiation between particular compounds could be observed, for example with D and E, ethanol caused a

decrease in resistance while methanol caused an increase in resistance.

F. to W. Sensors based on various organic polymers
5 directly deposited on a stainless steel electrode substrate

The table in Figure 6 shows further embodiments of semiconductor polymers. In each case the polymer was electrolytically deposited, the electrolyte being tetra-
10 ethylammoniumtetrafluoroborate and the monomer and electrolyte concentrations 0.1M except where stated otherwise. The anode was stainless steel. The voltage difference was 3 volts and the time of deposition was 10 minutes. In each case the polymer material was a black coating on the anode.
15 In these cases, using a stainless steel electrode most of the polymers formed good coatings directly on the metal.

Figure 7 shows traces obtained when a mixture of ethanol and iso-octane were injected into a gas liquid chromatograph in which the gas outlet was switched between a
20 flame ionisation detector and a polychloroaniline sensor made according to the present invention. The ionisation detector temperature was 210 degrees Celsius and the column temperature was 140°C with, as carrier gas, nitrogen at 3 millilitres/minute. The flame detector produced the
25 responses (a) and (b). The polychloroaniline sensor produced the characteristic (c) having a specific shape feature by which the presence of the ethanol was clearly

identified. There was no shape feature in response to iso-octane.

The gas-sensitive behaviour of the sensors of the present invention can be partially explained by the fact
5 that when a molecule of a gas becomes adsorbed on to the surface of one of these organic semiconductors, electrons may be donated to or withdrawn from the active surface and a change in electrical resistance can be observed due to the change in pi-electron density. Another contribution to the
10 change in resistance may be ascribed, at least in some cases, to conformational changes in the polymer molecule, involving disturbance of the conjugated pi-electron system. By modification of the chemical groups on the active surface of the polymer and by creating steric effects or group
15 specific effects selectivity to different types of gases can be achieved.

Applications

20 Some possible applications for sensors are:

(a) Monitoring of specific gases or odorant levels in industrial environments.

(b) Detectors for gas liquid chromatography.

(c) Quality control in the food and beverage industry
25 by monitoring the volatile components important in taste and smell.

(d) Objective measurements of components from

perfumery products.

A sensor of the present invention can be used in conjunction with other sensors to discriminate further the output from the earlier sensor system. In the example
5 illustrated in Figure 7, it might be difficult for example to identify with the flame ionisation detector whether ethanol or iso-octane is present if a single signal is produced. However, the sensor of the present invention will indicate which it is.

10 Put more generally; a gas identification system comprises using a first gas sensor to provide a first level of discrimination whereby the signal from the sensor indicates a range of possible gases, and using a second gas sensor to provide a second level of discrimination whereby
15 the signal from the sensor reduces said range of possibilities, and optionally using a third or higher number of sensors similarly to increase the level of discrimination and thereby more accurately indicate the nature of the gas detected.

20 As described, one or more of the gas sensors can be of a different type from the polymeric semiconductor sensor of the invention; for example a flame ionisation detector in combination with a polymeric semiconductor sensor. However, a plurality of semiconductor sensors of the present
25 invention may be used, either separately or simultaneously to provide a set of signals from the sensors, each being characteristic of the response of the respective semi-

conductor to the gas being detected, and each therefore providing a higher level of discrimination with respect to the collection of signals provided by the rest of the sensors.

5 The degree of discrimination required will vary according to the particular use to which the gas detector is put. With a sufficiently large number of different sensors, it may be possible to provide a "fingerprint" response, which, if encountered, will positively identify the gas in
10 any situation. In general, however, the particular circumstances of detection will have a bearing on the situation, so that detection is, in effect, from only a rather limited number of possible gases; and so rather fewer different sensors are needed to obtain a positive identification. For
15 example, in an extreme case, if only one contaminating gas were possibly present, it might be sufficient to employ a single semiconductor sensor with a known response to that gas. However, one can imagine, for example, testing a sample of ethyl alcohol for common contaminants using
20 sensors A to E indicated in Fig. 5. If the sample is chromatographed so as to separate the gases, the presence of methanol, butanol and ethyl acetate will be distinguished, but not acetic acid, which has the same response as ethanol. However, the addition of one or more sensors using polymers
25 which react differently to acetic acid and ethanol will increase the level of discrimination and enable acetic acid also to be identified. Alternatively, the chromatograph

itself may provide the first level of discrimination, so that although ethyl alcohol and acetic acid give the same response, their relative positions in the chromatograph may serve to distinguish between them and enable a positive
5 identification to be made.

In the food industry, for example, it may be required to detect the presence of just one particular substance known to be responsible for an undesirable "off" flavour. This can be detected by selecting one or more sensors which
10 react characteristically differently to that substance than to the flavours normally present in the foodstuff.

The signals from the sensors described above can be processed using the methods described by Persaud K. and Dodd G. in "Nature" (1982), Vol.299, pages 352-355.

15 In a modified form of sensor, the element is a coating of organic semiconductive polymer material on a gate field effect transistor. The change in conductivity of the element, when exposed to different ambient gases or odorants, can readily be detected as a change in capacitance
20 to give useful indications identifying such gases or odorants.

CLAIMS

1. A method of gas detection which comprises using a plurality of gas detectors each of which provides a characteristic response to the presence of a particular gas to be detected; the method being characterised by noting the response from each detector to the gas being detected so as to obtain a response pattern from the detectors collectively which provides a higher level of characterisation of the gas than is provided by any of the detectors individually, at least one of the detectors having a sensor comprising an organic polymeric semiconductor material which changes its electrical resistance in the presence of certain gases.
2. A method according to claim 1 wherein the organic semiconductor is selected from polypyrrole; polychloroaniline; polyisobutylthiazole; polyindole; poly-N,N-dimethylaniline; polyphenol; polymethylpyrrole; polyphenylenediamine; polyisovaleraldehyde-aniline (Schiff's base); polythiophene-2-acetonitrile; polyaniline; polynaphthylamine; poly-3,5-dimethylaniline; poly-2,6-dimethylaniline; poly-4-methylaniline; poly-N-hexylaniline; poly-2-anilinoethylacetate; poly-2-anilino-2-methylbutylacetate; poly-2-anilinomenthylacetate.
3. A method according to claim 1 or claim 2 wherein the polymer is formed on a substrate by electrolytic deposition

from a solution of monomeric material comprising a solvent medium in which the monomer is sparingly soluble.

4. A method according to claim 3 wherein the solution
5 comprises a protic medium and optionally one or more aprotic solvents.

5. A method according to claim 3 or claim 4 wherein the
solution comprises an ionic base.

10

6. A method according to claim 5 wherein the base is a quaternary ammonium compound.

7. A method according to claim 6 wherein the base is
15 tetraethylammoniumtetrafluoroborate.

8. A method according to any one of the preceding claims wherein one of said detectors is a flame ionisation detector.

20

9. A method according to any one of the preceding claims wherein a plurality of said detectors comprise different polymeric semiconductor materials.

25 10. A method according to any one of the preceding claims wherein one of said detectors is a gas chromatograph.

11. A method of producing an organic polymeric semiconductor material which comprises electrolytically depositing the polymer on a substrate from the solution of monomeric material, which solution comprises a solvent medium in which the polymer is sparingly soluble.
12. A method according to claim 11 wherein said medium includes a protic medium and optionally one or more aprotic solvents.
13. A method according to claim 11 or claim 12 wherein the solution contains an ionic base.
14. A method according to claim 13 wherein said base is tetraethylammoniumtetrafluoroborate.
15. An organic polymeric semiconductor material as made by a method according to any one of claims 11 to 14.
16. A polymer of claim 15 selected from polypyrrole; polychloroaniline; polyisobutylthiazole; polyindole; poly-N,N-dimethylaniline; polyphenol; polymethylpyrrole; polyphenylenediamine; polyisovaleraldehyde-aniline (Schiff's base); polythiophene-2-acetonitrile; polyaniline; polynaphthylamine; poly-3,5-dimethylaniline; poly-2,6-dimethylaniline; poly-4-methylaniline; poly-N-hexylaniline; poly-2-anilinoethylacetate; poly-2-anilino-2-methylbutylacetate; poly-2-

anilinomenthylacetate.

17. A sensor element comprising an organic polymeric semiconductor material of claim 15 or claim 16.

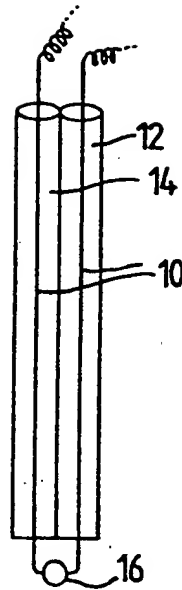
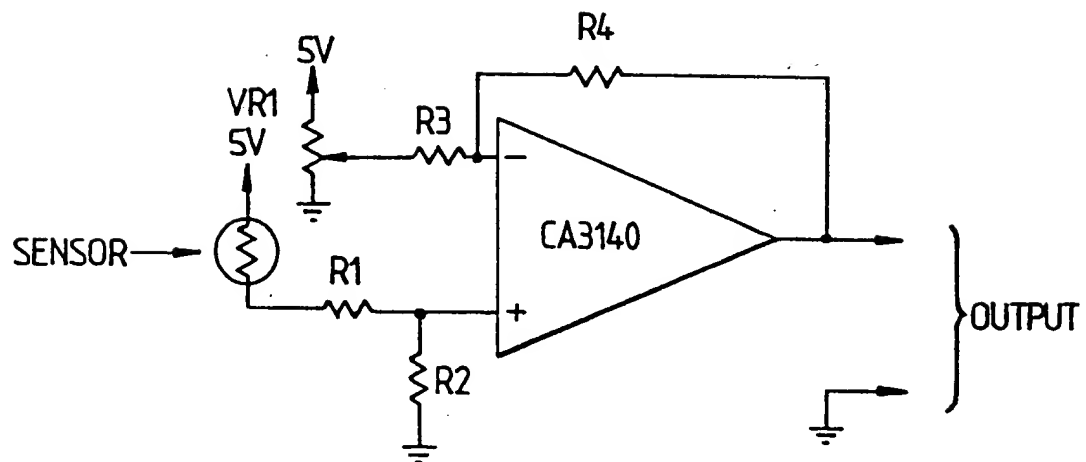
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18. A sensor element comprising an electrode substrate on which is electrolytically deposited a first layer of an organic polymeric semiconductor material whose electrical resistance changes in the presence of certain gases, and a
10 second layer of a different said organic polymeric semiconductor material electrolytically deposited on the first layer.

19. A sensor according to claim 18 wherein said first
15 layer is polypyrrole.

20. A sensor according to claim 18 or claim 19 wherein said layers are as made by a method of any one of claims 11 to 14.

20

Fig.1.*Fig.2.*

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Fig.3.

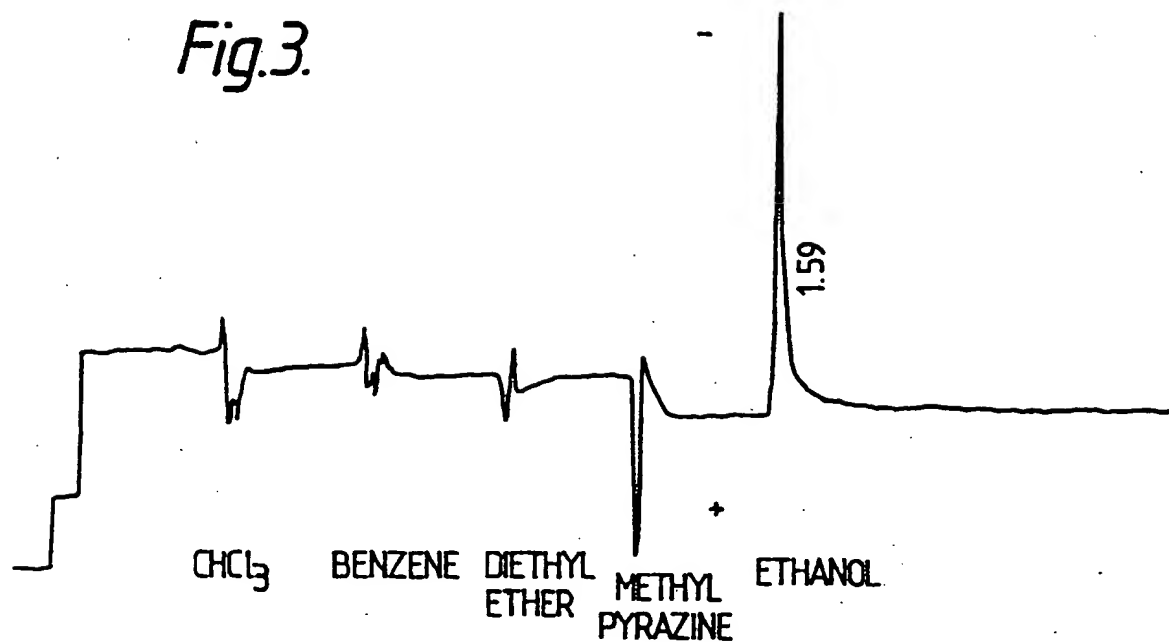
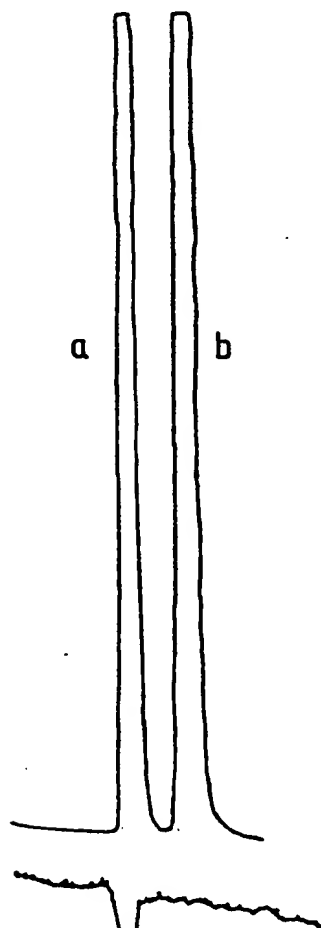
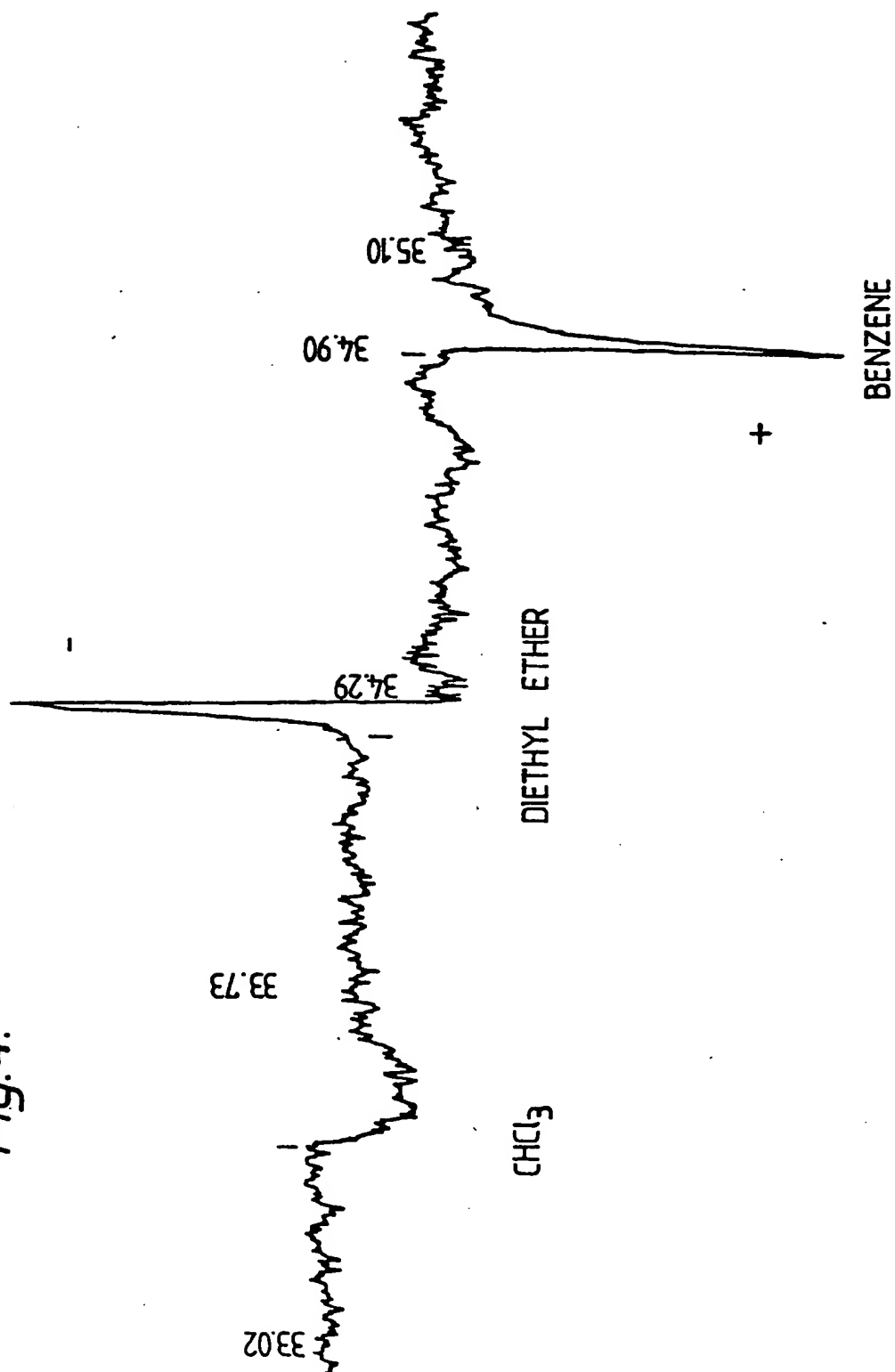


Fig.7



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Fig. 4.



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Changes in electrical resistance in different sensors in response to various compounds.

COMPOUND	SENSOR				
	A	B	C	D	E
ACETIC ACID	-	-	-	-	-
AMMONIA	+	-	+	-	+
BENZALDEHYDE	-	-	-	-	-
BENZENE	+	-	-	0	+
BROMINE	+	-	-	-	-
BUTANOL	-	0	0	-	0
CHLOROFORM	+	-	+	-	+
CYCLOHEPTANONE	-	0	-	0	0
1, 2-DIAMINOETHANE	+	+	-	-	+
DICHLOROMETHANE	-	+	-	-	0
DIETHYL ETHER	-	-	+	+	+
DIETHYL KETONE	-	-	+	-	-
ETHANOL	-	-	-	-	-
ETHYL ACETATE	-	0	-	0	+
GERANIOL	-	0	-	+	-
N-HEPTANE	-	0	0	0	0
HEXANOL	-	+	-	-	0
B-IONONE	-	-	-	+	-
2-MERCAPTOETHANOL	-	0	-	-	-
METHANOL	-	-	0	+	+
2-METHYL PYRAZINE	-	-	-	-	+
PHENYLETHANOL	-	0	-	-	0
α -PINENE	-	0	-	+	0
B-PINENE	-	0	-	+	0
PIPERIDINE	-	-	-	-	+
PYRIDINE	-	-	-	-	+
PYRROLIDINE	-	-	-	-	+
TRIETHYLAMINE	-	-	-	+	+

(+) Increase in resistance, (-) Decrease in resistance, (0) Negligible response

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FIG. 6

Embodiment	Monomer	Solvent	Comments
F	N,N-dimethylaniline	82% EtOH	Easy polymerization. Regular and compact black coating. The solution becomes dark.
G	2-chloroaniline	90% EtOH	The polymer partly goes in solution, while it forms, and is thin but regular.
H	2-chloroaniline	70% EtOH	Easy polymerization.
I	3-chloroaniline	70% EtOH	The polymer forms very slowly.
J	Phenol	57% AcN	The polymer forms well. The solution becomes yellow. Monomer conc. 0.24 M; electrolyte conc. 0.071 M.
K	Indole	80% EtOH	Easy and quick polymerization.
L	Aniline	70% EtOH	The polymer forms well, but is brittle.
M	1-methylpyrrole	99% AcN	Easy and quick polymerization.
N	1-naphthylamine	50% EtOH	The polymer forms well. The solution turns from violet to brown.
O	m-phenylenediamine	70% EtOH	Polymer black and regular.
P	Isovaleraldehyde-aniline	90% EtOH	The polymer forms well. Monomer conc. 0.024 M.
Q	N-hexylaniline	70% EtOH	Thin but compact.
R	3,5-dimethylaniline	40% EtOH	Thin, but regular. 0.05 M electrolyte conc.
S	2,6-dimethylaniline	20% EtOH	Brittle.
T	4-methylaniline	50% EtOH	Brittle, not regular. Partly dissolves.
U	2-anilinoethylacetate	50% EtOH	Brittle.
V	2-anilino-2-methylbutylacetate	70% EtOH	Brittle.
W	2-anilinomethylacetate	80% EtOH	Thin and brittle.
EtOH = ethyl alcohol		AcN = acetonitrile	

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 85/00373

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: G 01 N 27/12

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System

Classification Symbols

IPC⁴ G 01 N 27/00
C 08 G 61/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁸

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	DE, A, 3217883 (SIEMENS) 17 November 1983, see page 6, paragraphs 1,2; pages 8-11 ---	1
X	EP, A, 0098988 (BASF) 25 January 1984, see page 4, line 32 - page 11, line 2 ---	11-20 2-7
A	EP, A, 0022028 (COMPAGNIE CENTRALE SICLI) 7 January 1981, see page 4, line 18 - page 7, line 18; page 16, lines 1-12 (cited in the application) ---	1-3,11,15- 17
A	US, A, 3428892 (J.E. MEINHARD) 18 February 1969, see column 1, line 55 - column 3, line 8 -----	1,2,9

* Special categories of cited documents: ¹⁴

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

25th November 1985

Date of Mailing of this International Search Report

18 DEC. 1985

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

G.L.M. Krieger

INTERNATIONAL APPLICATION NO. PCT/GB 85/00373 (SA 10429)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/12/85

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A- 3217883	17/11/83	None	
EP-A- 0098988	25/01/84	DE-A- 3223545	29/12/83
		JP-A- 59008723	18/01/84
		US-A- 4532188	30/07/85
EP-A- 0022028	07/01/81	FR-A, B 2460480	23/01/81
		AT-B- E7174	15/05/84
US-A- 3428892	18/02/69	DE-A, C 1805624	27/05/70
		FR-A- 1591669	04/05/70